

Synthesis and Characterization of Polyimide/Hexagonal Boron Nitride Composite

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ABSTRACT: Polyimide (PI)/hexagonal boron nitride (h-BN) composites were produced via the thermal imidization procedure from solution mixtures of a polyamic acid, which is prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 3,3'-diaminodiphenyl sulfone (DADPS) in *N*-methyl-2-pyrrolidone (NMP), and alkoxy-silane functionalized h-BN. The structure, thermostability, thermal behavior, and surface properties of the resulting materials were characterized by means of Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM). The thermal

characteristics of PI/h-BN films were better than the pure PIs. The physical and mechanical properties of the films were evaluated by various techniques such as contact angle, chemical resistance, and tensile tests. The flame retardancy of the composite materials was also examined by the limiting oxygen index (LOI). The experiments showed that the LOI values of PIs increased from 32 to 43 for the materials containing hexagonal boron nitride. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 706–712, 2012

Key words: hexagonal boron nitride; composite; polyimide; h-BN; LOI

INTRODUCTION

Boron nitride is a ceramic material that is isoelectronic with carbon. Much like carbon, it exists in multiple allotropic forms. The most common structure of boron nitride is the hexagonal form (h-BN).¹ Hexagonal boron nitride (h-BN) has a graphite-like structure with strong bonding within the planar, fused, six-membered rings, and weak van der Waals bonding in-between layers. Along the *c*-axis for h-BN, boron and nitrogen atoms are stacked above each other in alternating layers.^{2,3} Because of its properties, it has found uses in heat conductivity applications, electrical insulation applications, corrosion resistance applications, lubrication applications, personal care applications, and as a plastic additive.⁴ The increased use of h-BN powder as a performance-enhancing additive to plastics has increased the importance of understanding its surface characteristics. For filled polymer composites, the nature of the interfacial region can significantly influence properties due to substantial interfacial areas introduced by

filler incorporation. Knowledge about the filler surface is, therefore, essential in order to understand and control the interfacial interactions with a polymer.²

Aromatic polyimide (PI) films have attracted a great deal of interest as one of the prominent precursors for producing carbon and graphite films in recent years.⁵ Aromatic PI is well known as a high-performance engineering polymer. Compared to most organic polymeric materials, PI exhibits superior thermal stability and mechanical strength.⁶ Therefore, a large number of PI compositions have been extensively investigated, and most of them are well-suited for use as matrix resins, adhesives, and coatings for high-performance applications in the aerospace, electric, and microelectronic industries.^{7,8}

Organic–inorganic nanocomposites have proven to be new advanced materials, because they combine the advantages of organic components (e.g., flexibility, low dielectric constant, and process ability) and inorganic components (e.g., rigidity, durability, and thermal stability). Hybridization with inorganic compounds has been focused on the modification of polyimides to improve their thermal, physical and mechanical properties.^{7–9}

It is well known that h-BN possesses a number of interesting properties such as lubrication action, low hardness, and low friction coefficient. However, it has not reported yet, the effect of h-BN on the thermal and mechanical properties of PIs.^{10,11} In the

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present study, PI/h-BN composite materials were prepared from a polyamicacid (PAA) (PI precursor) and h-BN that is modified with aminoalkoxysilane. The aminoalkoxysilane is one of the most widely applied silane-coupling agents for the modification of various oxide surfaces. This agent is used for the surface treatment of the filler to improve the affinity between filler and matrix, thereby significantly increasing the thermal properties of the composite. The morphological, mechanical, and thermal properties of the PI films with different h-BN content were characterized.

EXPERIMENTAL

Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Merck. 3,3'-Diaminodiphenyl sulfone (DADPS) was obtained from Merck and recrystallized from ethanol before use. *N*-methyl-2-pyrrolidone (NMP) was supplied by Merck, and it was dried and freshly distilled over phosphorous pentoxide (P_2O_5) before use. h-BN was supplied from Henkel. Their powders were dried and degassed under vacuum (10^{-2} torr) at 300°C several hours before use. A silane-coupling agent *N*-(β -aminoethyl)- γ -amino propyl-trimethoxysilane (Z-6020) was purchased from Dow Corning. Ethanol was obtained from Merck. Glass panels ($50\text{ mm} \times 100\text{ mm} \times 2\text{ mm}$) were used as a substrate to prepare free thin films.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectrum was recorded on Perkin Elmer Spectrum 100 ATR-FTIR spectrophotometer. The morphology of the composite materials was examined using scanning electron microscopy (SEM; JEOL JSM-5910 LV). The fractured surfaces were coated with a gold layer by vacuum sputtering.

Thermogravimetric analyses (TGA) of the free films were performed using a Perkin-Elmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 to 750°C with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen and air atmosphere.

The thermal properties were characterized by differential scanning calorimetry (DSC) analyses, which were performed on Perkin-Elmer Diamond DSC. Two runs from 30 to 300°C with a heating rate of $10^\circ\text{C}/\text{min}$ were performed.

The limiting oxygen index (LOI) values of the composite materials were measured using a Fire Testing Technology type instrument on the test specimen bar of $120 \times 60 \times 3\text{ mm}^3$ according to ASTM D2863-08.

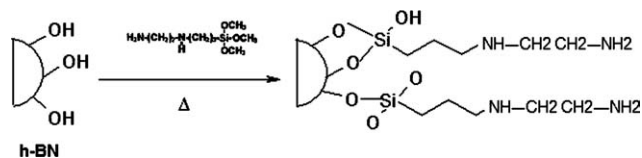
The wettability characteristics of free films were performed on a Kruss (Easy Drop DSA-2)

tensiometer. A sessile drop method was used to measure a contact angle (θ) of a $3\text{--}5\ \mu\text{L}$ distilled water.

Mechanical properties of the free films were determined by standard tensile stress-strain tests to measure modules, ultimate tensile strength, and elongation at break. Standard tensile stress-strain experiments were performed at room temperature on Materials Testing Machine Z010/TN2S, using a cross-head speed of $5\text{ mm}/\text{min}$.

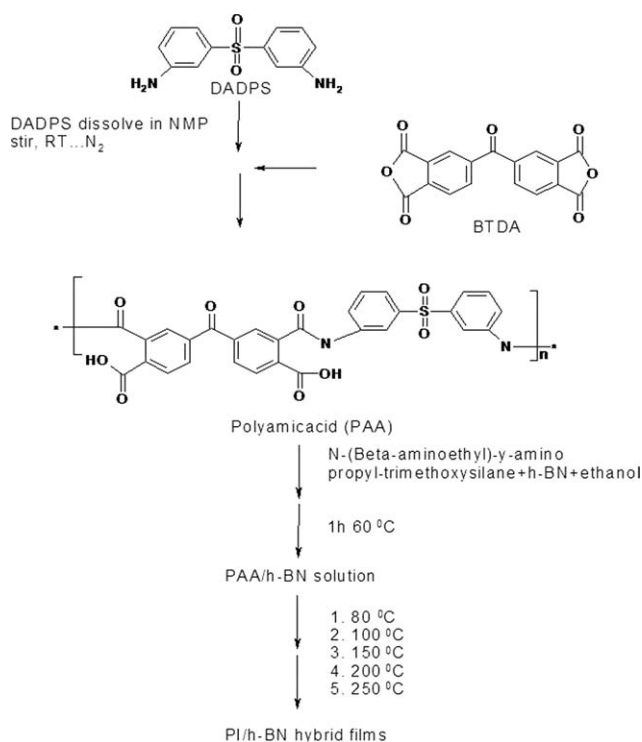
h-BN filler functionalization

N-(β -aminoethyl)- γ -amino propyl-trimethoxysilane was dispersed in ethanol for 10 min at 60°C . The hexagonal boron nitride (h-BN) was added to the solution and allowed to mix for 1 h . Then, the product was filtered, washed with alcohol, and dried in an oven for 12 h at 110°C .^{12,13}



Preparation of PI/h-BN composite films

PAA that is used as a polyimide (PI) precursor was prepared in NMP. Briefly, DADPS (0.01 mol , 2.485



Scheme 1 Preparation of polyimide composite films.

TABLE I
The Recipe for the Preparation of Formulations

Sample	DADPS (g)	BTDA (g)	NMP (mL)	Functionalized h-BN (g)
PI (control)	2.485	3.220	28.5	–
PI/h-BN 0.5	2.485	3.220	28.5	0.1
PI/h-BN 1	2.485	3.220	28.5	0.2
PI/h-BN 2	2.485	3.220	28.5	0.4

g) was dissolved in 28.5 mL of dried NMP. Then, BTDA (0.01 mol, 3.220 g) was added in small portions. The resulting solution was stirred for 24 h at

room temperature under N_2 atmosphere. The solid content of PAA solution was kept at about 20% (w/v). Various amounts (0, 0.5, 1, and 2 wt %) of functionalized h-BN were added into the PAA solution with vigorous stirring to minimize the occurrence of local precipitation. After stirring for 1 h, the reaction is completed. After mixing through stirring, the obtained white color solution was cast on to the glass plates with the aid of a 30- μm applicator. Then, the wet coating was cured at 80, 100, 150, 200, and 250°C for 1 h at each temperature. The cured films were retrieved from the glass surface by immersing in distilled water at 80°C.

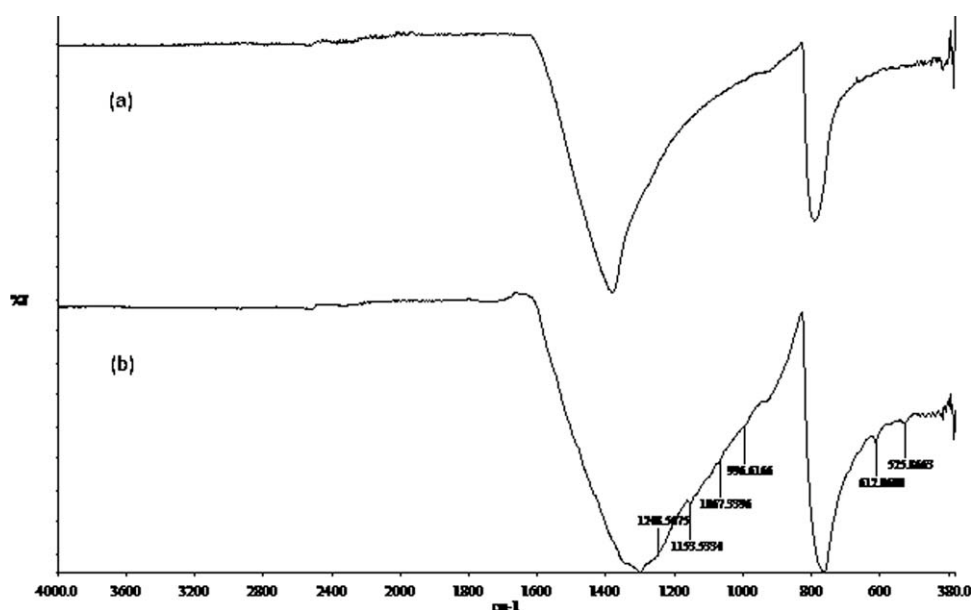


Figure 1 FTIR spectra of (a) h-BN and (b) amino silane modified h-BN.

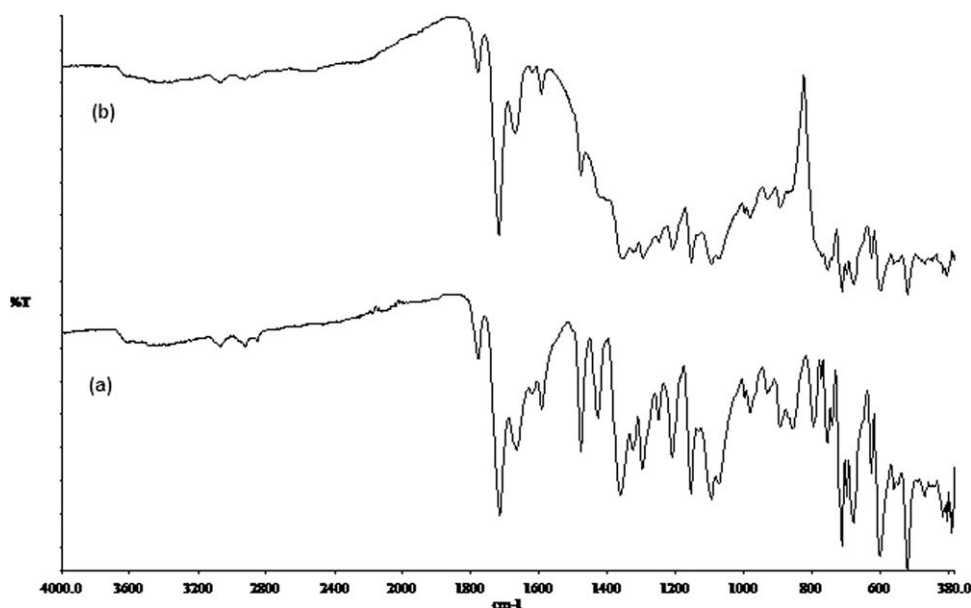


Figure 2 FTIR spectra of (a) PI and (b) PI/h-BN 2.

RESULTS AND DISCUSSION

In the present study, a series of PI (pure PI and control sample) and PI/h-BN composite materials were prepared. In Scheme 1, the preparation of PI/h-BN composite materials from PAA solution (BTDA and DADPS in NMP) and functionalized h-BN is shown. Totally, four samples with each have different amounts of h-BN content, in the range of 0–2 wt % were prepared. The recipe of the preparation of formulations was shown in Table 1.

In these composite systems, PI was used as an organic polymer matrix, and functionalized h-BN was acted as inorganic filler.

The ATR-FTIR spectra of both h-BN powders treated with a silane-coupling agent and the untreated powders were shown in Figure 1. The h-BN was characterized by two prominent bands at 1381 cm^{-1} and 791 cm^{-1} , corresponding to B–N stretching and B–N bending, respectively. The absorption bands in the 1000 and 1200 cm^{-1} region indicate the characteristic Si–O–C bonds.^{12–17} The ATR-FTIR spectra for PI and PI/h-BN-free film containing 2 wt % of h-BN were shown in Figure 2. Both samples exhibited the characteristic peaks of symmetric and asymmetric C=O stretching of the imide group at 1720 and 1780 cm^{-1} , respectively. Additionally, C–N stretching of the imide ring and C=C stretching vibration of the phenyl groups were observed at 1361 and 1606 cm^{-1} , respectively. After the introduction of the functionalized h-BN, the strong absorption bands can be observed in the range of 830 – 870 cm^{-1} corresponding to Si–O–Si network formation.^{9,12–18}

The morphology of the fractured surfaces of the composite films with different h-BN content was observed by SEM. Figures 3 and 4 show that h-BN fine flakes are homogeneously dispersed throughout the PI matrix, but the h-BN particles are relatively large and debonded from the surrounding PI matrix, indicating relatively poor compatibility between the PI and h-BN phases.

The thermal stability of PI and PI/h-BN free films is measured under air and nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. As can be seen from Table 2, there are two main weight losses in all the samples. Under both atmospheres, the temperatures at 5% weight loss ($T_5\%$'s) were started at about 300°C due to the PI can be assigned to incomplete imidization. The second one that corresponds to main degradation step was observed at 523 – 534°C under nitrogen and at 582 – 591°C under air. As shown in Figure 5 and Table 2, the maximum decomposition temperature of the samples increases with the increasing h-BN content of the PI composite films. The char yields at 750°C were also collected. The experimental results show that h-BN plays a role in

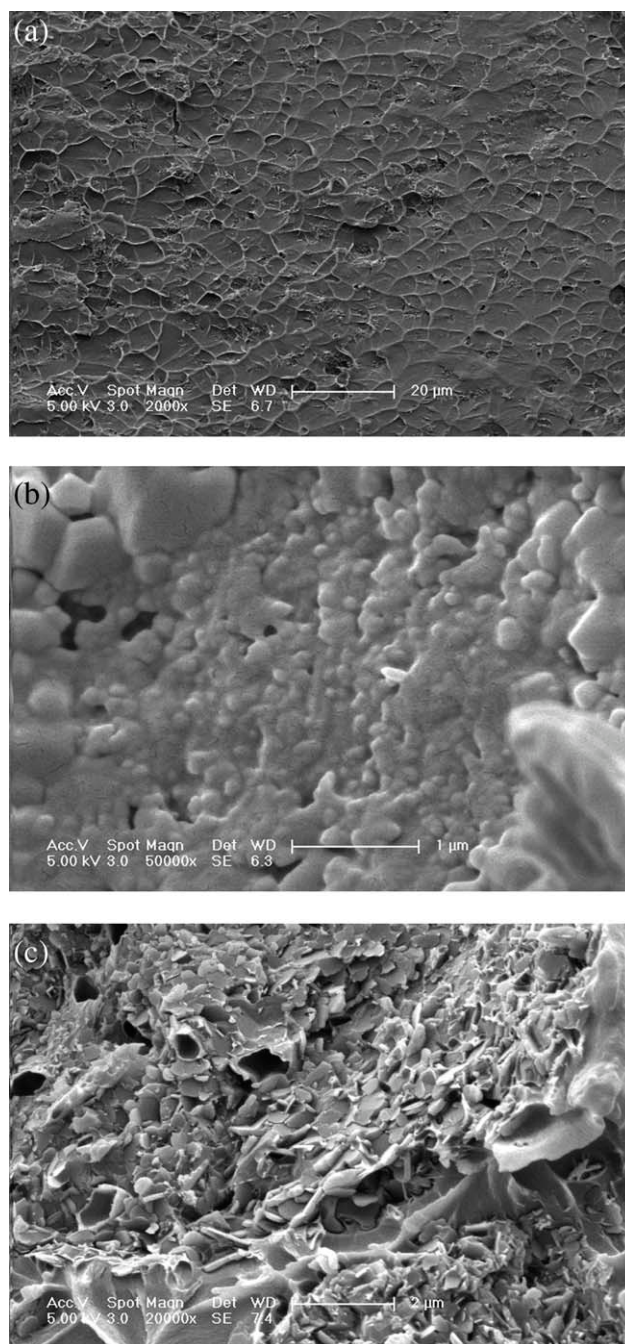


Figure 3 SEM micrographs of (a) PI/h-BN 0.5×2000 ; (b) PI/h-BN $0.5 \times 50,000$; (c) PI/h-BN $0.5 \times 20,000$.

char formation, and the char yield has been correlated to flame retardancy. The activation energy E_a for the oxidation of h-BN is higher than carbon, which means that h-BN has higher thermal stability than carbon. Thus, h-BN protects the polymer chains trapped in the network from a thermo-oxidative process.¹⁹

The flame retardancy of the materials was examined by the LOI. Figure 6 shows that the LOI values increased from 32.0 to 42.6 for the free films.

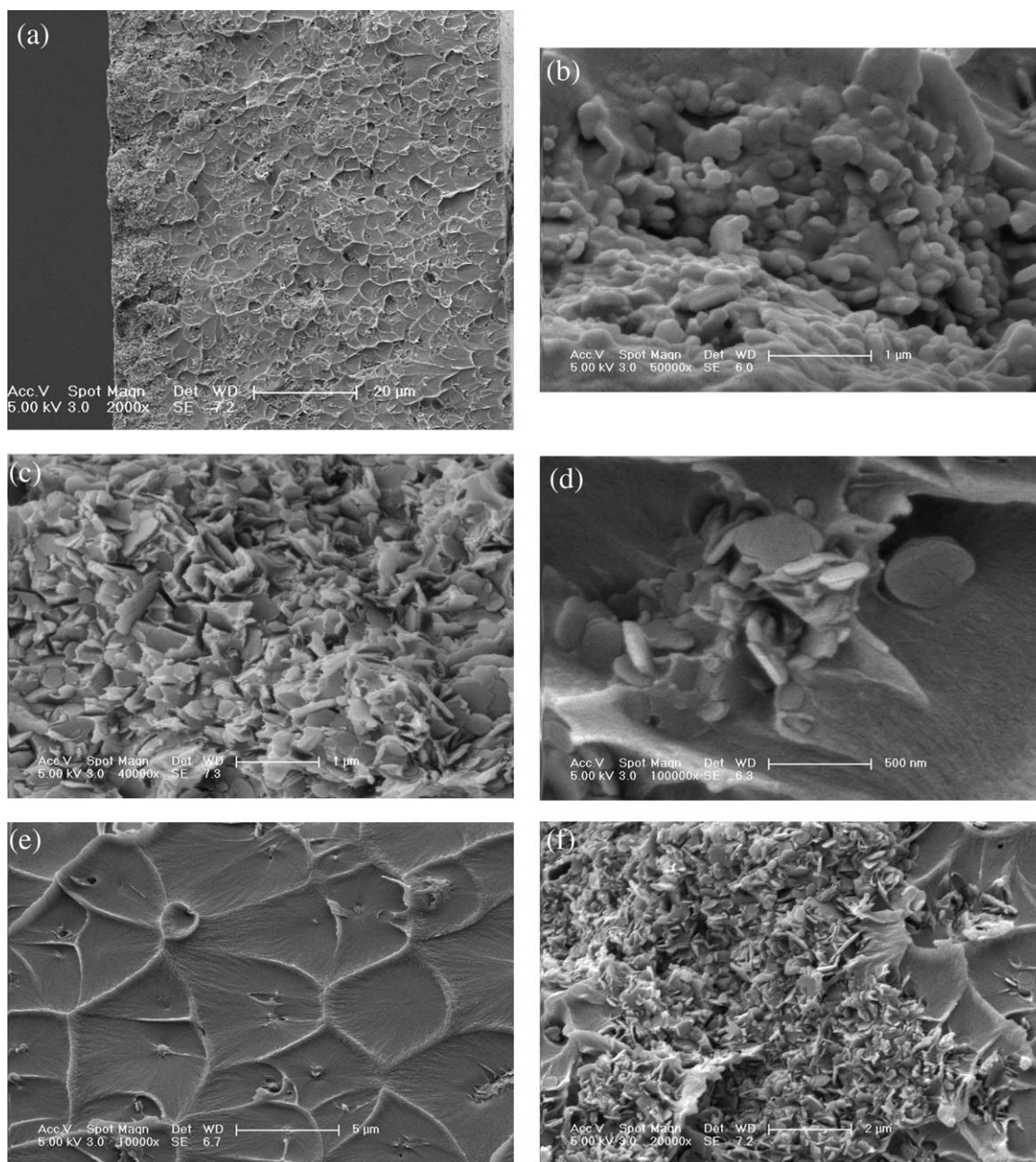


Figure 4 SEM micrographs of (a) PI/h-BN 1 × 2000, (b) PI/h-BN 1 × 50,000; (c) PI/h-BN 1 × 40,000; (d) PI/h-BN 1 × 100,000; (e) PI/h-BN 1 × 10,000; (f) PI/h-BN 1 × 20,000.

Consequently, the h-BN-containing composite materials show fire resistance than the pure PI.

Table 2 depicts the T_g values obtained from the DSC experiments. As it can be seen from Table 2

that the T_g values of the materials increased with the increase in h-BN content. T_g is an important parameter in connection with the structures and properties of polymers. In general, the T_g value is strongly

TABLE II
Thermal Properties of Polyimide Films

Sample	T_5 (°C)		Max. weight loss (°C)		Char yield (%)		T_g (°C)
	In air	In N ₂	In air	In N ₂	In air	In N ₂	
PI (control)	296	286	582	523	0.8	53.7	227
PI/h-BN 0.5	297	297	586	525	4.0	54.2	228
PI/h-BN 1	303	301	588	531	6.7	55.7	229
PI/h-BN 2	311	302	591	534	9.5	56.6	230

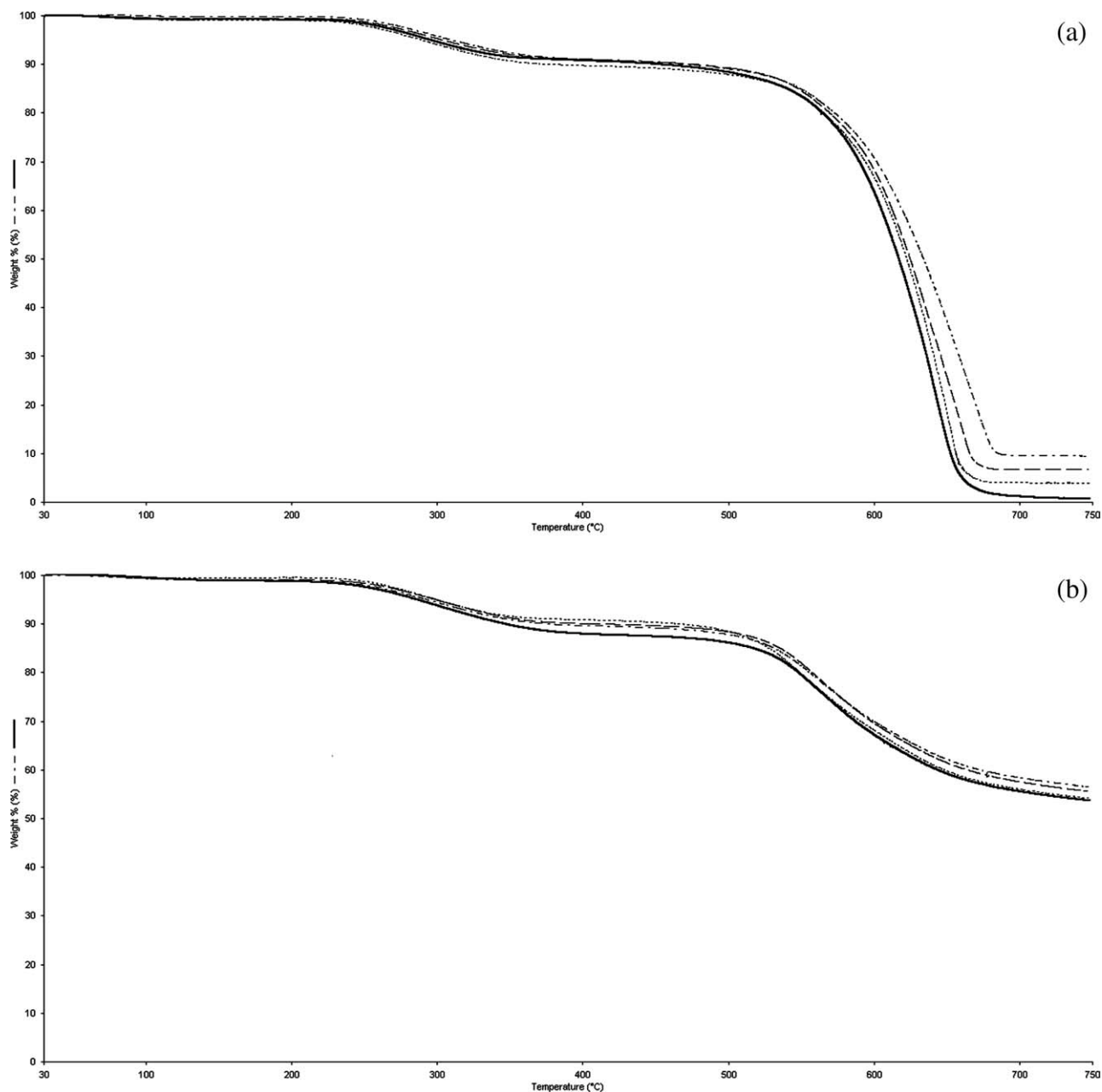


Figure 5 TGA curves of polyimide at (a) air atmosphere; (b) nitrogen atmosphere.

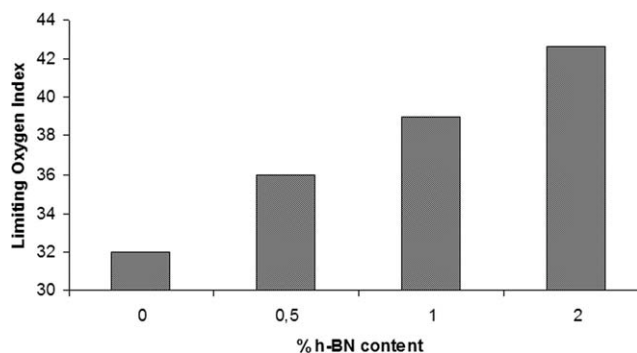


Figure 6 LOI values of polyimide films.

influenced by the polymeric chain flexibility, molecular weight, and length of the spacer group. In this study, with an increase in the concentration of modified h-BN, the space steric hindrance increased, making the chain flexibility decrease; therefore, the mobility of chain segments decreased and the T_g value slightly increased. As we know, T_g involves the mobility of chain segments, and the T_g value increases with a decrease in the mobility of chain segments.

The mechanical properties of PI and PI/h-BN composite films with the h-BN contents of 0, 0.5, 1, and 2 wt % are depicted in Table 3. There was a systematic decrease in the modulus, elongation at

TABLE III
The Mechanical Properties of Polyimide Films

Samples	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PI (control)	1867	655	4.70
PI/h-BN 0.5	1671	620	3.55
PI/ h-BN 1	1625	474	3.23
PI/ h-BN 2	1602	470	3.01

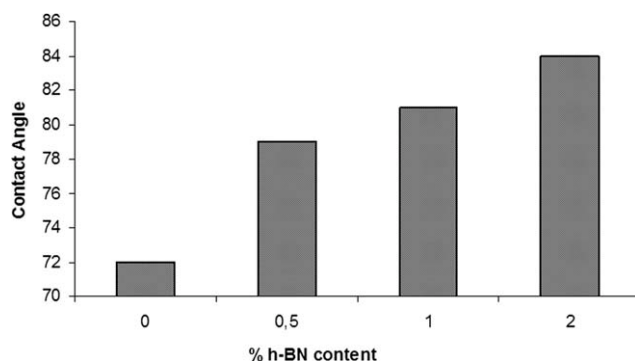


Figure 7 Contact angle values of polyimide films.

break, and tensile strength with the increase in h-BN content of the free films. The elastic moduli of PI and PI/h-BN 0.5 are 1867 and 1671 MPa, respectively. The decrease in the elastic modulus of PI was expected and that caused the weak interface between h-BN and PI.²⁰ The slight decrease in elongation may be due to the increased crosslinking density by the formation of organic-inorganic network (Si—O—Si) structure. Under applied stress, because of the restricted movement of chains, strain will drastically reduce.

The contact angle is the angle at which a liquid interface meets the solid surface. Each contact angle value given in Figure 7 represents an average of five to seven readings. As it can be seen from Figure 7, there is a slight enhancement in contact angle results as the inorganic content of the coating increases orderly. This is an expected behavior assuming that h-BN makes the surface more hydrophobic.

The chemical resistance of all composite films was also investigated by immersing samples in various reagents (37% HCl, 65 % NaOH, xylene, toluene, and acetone) for 24-h time period. The general

physical appearance of samples was perfect, and no cracks were observed.

CONCLUSIONS

In this study, h-BN-containing PI composite materials were prepared by thermal imidization technique. The thermal stability of the materials improved with the increasing amount of h-BN in the compositions. The LOI values increased from 32.0 to 42.6. The h-BN-containing composite materials show more fire resistance than the pure PI. The SEM morphological study proved that the h-BN fillers in the PI matrix are dispersed homogeneously. The results showed that the lubricating and low hardness properties of h-BN additives made the PIs with low modulus. The solvent and chemical resistance experiments for all materials show good performance.

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